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(54) HYDROPHILIC POLYURETHANES USABLE IN DETERGENT COMPOSITIONS

(71) We, RHONE-POULENC INDUSTRIES, a French Body Corporate, of 22, Avenue Montaigne, 75 Paris 8eme, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to hydrophilic linear polyurethanes of high molecular weight, and their use as anti-redeposition, anti-soiling and antistatic agents.

Polyesters containing acid groups or hydrophilic polymeric groups which can give rise to solvation with water, which are particularly effective as anti-redeposition agents, have been described in French Patent No. 1,499,508. This patent describes, particularly, the polyesters resulting from the polycondensation of phthalic acid with a low molecular weight glycol and a polyoxyalkylene glycol. In this way a polyester molecule is formed comprising hydrophobic units made up of phthalic acid/low molecular weight glycol chains and hydrophilic units derived from polyoxyalkylene glycol groups. The bond between these units is provided by forming an ester group from an acid group and an alcohol group, the reaction taking place at a temperature above 200°C. The products thus obtained have a relative viscosity of 1.1 to 1.5.

By "relative viscosity" is meant: the ratio of the flow time of a given volume of a 1% strength by weight solution of the polymer in *ortho*chlorophenol through a calibrated capillary tube, to the flow time of the same volume of *ortho*chlorophenol through the same apparatus, the measurements being carried out at 25°C.

We have now synthesised, according to the present invention, products which possess hydrophobic and hydrophilic units, the bond between these units being provided by a urethane group which confers on the polyurethanes thus obtained a set of properties which are particularly useful in detergent compositions.

This invention provides a hydrophilic, linear polyurethane resulting from the reaction of 5 to 70, generally 10 to 70, % by weight of a linear hydroxyl-terminated polyester derived from terephthalic acid or a diester thereof, said polyester having an acid number of less than or equal to 3 mg of KOH/g and a hydroxyl number of not more than 120 mg of KOH/g, with from 95 to 30, generally 90 to 30, % by weight of a prepolymer with terminal isocyanate groups, obtained by the reaction of at least one hydrophilic non-ionic macrodiol which is polyethylene glycol, with at least one diisocyanate, the overall (i.e. polyester and prepolymer) molar ratio NCO to OH being at least 0.8 but less than 1, the polyurethane possessing a molecular weight such that the

relative viscosity of a 1% strength by weight solution of the polymer in *ortho*chlorophenol is at least equal to 2 at 25°C.

The polyester with terminal hydroxyl groups and whose acid number is less than or equal to 3 can be prepared in known manner, by any polyesterification reaction starting from at least one diacid, or a diester or anhydride thereof, at least a part of which is terephthalic acid or a diester thereof, and from at least one low molecular weight diol which does not confer a marked non-ionic hydrophilic character on the polyester.

As diacids it is possible to use, with the terephthalic acid or diester thereof, saturated or unsaturated aliphatic diacids and aromatic diacids, such as succinic, adipic, suberic and sebacic acid, maleic, fumaric and itaconic acid, *ortho*phthalic and isophthalic acid. Anhydrides of these acids can be used as well as their diesters. Suitable diesters include the methyl, ethyl, propyl or butyl diesters.

As diols, it is possible to use the aliphatic glycols such as ethylene glycol, diethylene glycol and the higher homologues having a molecular weight less than or equal to 300, propane-1,2-diol, dipropylene glycol and the higher homologues, butane-1,4-diol, hexane-1,6-diol, neopentylglycol, and cycloalkane glycols such as cyclohexanediol and dicyclohexanediolpropane.

In certain cases, for practical reasons, such as the handling of products in concentrated solution, it is of value to impart to the polyester a slight ionic character. In order to do this, a minor quantity of a sulphonated diacid can be incorporated when preparing the polyester, for example by introducing, in known manner, 5-sulpho-isophthalic acid or its methyl diester, in the form of one of their alkali metal salts.

In general terms, the ratio of the molar quantity of sulphonated diacid (when used) to the total molar quantity of diacids involved in the preparation of the polyester is less than or equal to 15%.

The preferred polyesters are those prepared from terephthalic acid or one of its diesters alone. They preferably have a number-average molecular weight of from 1,000 to 4,000, which corresponds to a hydroxyl number I_{OH} of from 25 to 120 mg of KOH/g. Typically the polyester is obtained from terephthalic acid or a diester thereof, alone or as a mixture with adipic acid or a diester thereof, and at least one of ethylene glycol, diethylene glycol or a higher homologue thereof of molecular weight at most 300, butane-1,4-diol or propane-1,2-diol.

The prepolymer with terminal isocyanate groups is prepared by reacting at least one non-ionic hydrophilic macrodiol which is polyethylene glycol with at least one diisocyanate.

The polyethylene glycol is one whose number-average molecular weight is generally from 300 to 6,000 and preferably from 600 to 4,000.

Organic, aromatic, aliphatic or cycloaliphatic diisocyanates are suitable. However, some of these are more commonly used than others because of their current availability. This applies essentially to the toluene diisocyanates, hexamethylene diisocyanate, isophorone diisocyanate and di-(isocyanatophenyl)-alkanes, such as di-(isocyanatophenyl)-methane, and the di-(isocyanatocyclohexyl)-alkanes, such as di-(isocyanatocyclohexyl)-methane.

The relative molar quantity of diisocyanate to be used relative to the overall quantity of macrodiol and of polyester depends on the molecular weight of the polyurethane end product that it is desired to obtain. In general terms the percentage by weight of diisocyanate in the polyurethane end product is from 2 to 15%.

Since, in general, it is desirable to obtain an end product with a high molecular weight, the molar ratio of NCO groups to the sum of the hydroxyl groups employed is at least 0.8 but less than 1.

To prepare the polyurethanes, it is possible to prepare, at atmospheric pressure, on the one hand, in a first reactor, the polyester, by a known method, and maintain it in the molten state, and on the other hand, in a second reactor, to prepare the prepolymer from the hydrophilic macrodiol and a diisocyanate, the temperature being just sufficient to maintain it in the molten state.

In this second reactor a temperature of 25 to 70°C is generally sufficient. Preferably, the reaction is effected under an atmosphere of nitrogen.

The prepolymer is then added to the polyester and the temperature is suitably maintained at 150 to 200°C, the pressure being atmospheric pressure, until the reaction has finished, that is to say until the viscosity becomes constant.

If a suitable installation is available, the various operations can be carried out continuously. The mixing of the polyester and the prepolymer with terminal isocyanate

groups can be carried out by means of metering pumps. The reaction can then be finished on a conveyor belt consisting of a material to which the end product does not adhere, such as polytetrafluoroethylene, marketed under the Registered Trade Mark "TEFLON".

When the process is carried out in reactors, it is desirable, for reasons of ease of agitation and drawing off the product, not to exceed a certain viscosity; nevertheless, with this type of apparatus, it is possible to prepare polymers with a relative viscosity, measured in a 1% strength by weight solution of polymer in *ortho*chlorophenol, at 25°C, of up to 4.

The following Examples further illustrate the invention. All parts and percentages are by weight unless otherwise stated.

In these Examples the molar ratio NCO/OH of the material reacted was at least 0.8 but less than 1. It will be appreciated that during the preparation of the polyurethane the heating used causes some volatilisation of the isocyanate-terminated prepolymer. Accordingly it may be necessary to introduce a small excess of isocyanate-terminated prepolymer; this excess can be determined experimentally to ensure that the final product does not contain any free NCO groups. This is why in certain of the Examples there is a theoretical excess of isocyanate.

EXAMPLE 1.

A. *Preparation of the polyester.*

In a reactor R_1, a polyester is prepared from:

	Parts	Molar proportions
Dimethyl terephthalate	333.8	5
Adipic acid	175.9	3.5
Dimethyl isophthalate 5-sodium sulphonate	152.8	1.5
Ethylene glycol	245.4	11.5

The condensation is carried out as a conventional polyesterification, the catalyst being tetraisopropyl *ortho*titanate.

The final condensation conditions are 220°C for the temperature and 20 mm of mercury for the pressure.

In this way 700 parts of a polyester were obtained, the properties of the polyester being as follows:

Acid number (I_a)	0.5 mg of KOH/g
Hydroxyl number (I_{OH})	29.9 mg of KOH/g
Average molecular weight ($\overline{M}n$)	3,764.

B. *Preparation of prepolymers with terminal isocyanate groups.*

300 parts of polyethylene glycol of molecular weight 600 are introduced into a reactor R_2, under an atmosphere of nitrogen. The material is heated to 50°C and 115.5 parts of hexamethylene diisocyanate are introduced all at once.

The reaction is allowed to continue for 1 hour at a temperature of 70°C.

C. *Preparation of the polyurethane.*

The temperature of reactor R_1 having been brought to 190°C, the contents of reactor R_2 are run into reactor R_1 in about 30 minutes, and the prepolymer is allowed to react with the polyester for about 45 minutes at this same temperature.

1,115.5 parts of a polyurethane with a relative viscosity, measured as indicated previously, of 2.05, are obtained.

EXAMPLE 2.

A. *Preparation of the polyester.*

In a reactor R_1, a polyester is prepared according to the method described in Example 1, from:

	Parts	Molar proportions
Dimethyl terephthalate	257.4	8.5
Dimethyl isophthalate 5-sodium sulphonate	69.3	1.5
Ethylene glycol	241.7	25

The final condensation conditions are a temperature of 240°C and a pressure of 20 mm of mercury.

330 parts of a polyester were obtained, the properties of the polyester being as follows:

Acid number (I_A)	0
Hydroxyl number (I_{OH})	57.4 mg of KOH/g
Number-average molecular weight ($\overline{Mn}$)	1,951.

B. *Preparation of the prepolymer with terminal isocyanate groups.*

670 parts of polyethylene glycol of molecular weight 4,000 are introduced into a reactor R_2, under an atmosphere of nitrogen, and are heated to 70°C. 58 parts of toluene diisocyanate (a commercial mixture of the 2,4 and 2,6 isomers in proportions of 80% and 20% respectively), are added all at once.

The reaction is allowed to continue for about 30 minutes at a temperature of 70°C.

C. *Preparation of the polyurethane.*

Following the procedure of Example 1, the prepolymer, prepared in Example 2B, is run into the polyester of Example 2A.

1,058 parts of a polyurethane with a relative viscosity, measured as previously indicated, of 2.1 are obtained.

EXAMPLE 3.

As described in Example 1C, a prepolymer with terminal isocyanate groups prepared by reacting 750 parts of polyethylene glycol of molecular weight 1,500 and 109 parts of toluene diisocyanate (a commercial mixture as described previously), is run into 250 parts of the polyester prepared in Example 2A.

1,109 parts of a polyurethane with a relative viscosity, measured as indicated previously, of 2.31, are obtained.

EXAMPLE 4.

A. *Preparation of the polyester.*

A polyester is prepared according to the method described in Example 1 from the following constituents:

	Parts	Molar proportions
Dimethyl terephthalate	236.9	10
Ethylene glycol	227.1	30

The polyesterification is finished at 240°C under a pressure of 20 mm of mercury.
250 parts of a polyester are obtained, the properties of the polyester being as follows:

Acid number (I_a)	0
Hydroxyl number (I_{OH})	60.9 mg of KOH/g
Number-average molecular weight ($\overline{Mn}$)	1,839.

B. *Preparation of the prepolymer with terminal isocyanate groups.*
The prepolymer is prepared from: 750 parts of polyethylene glycol of molecular weight 1,500 and 111 parts of toluene diisocyanate (the commercial mixture previously described).
The working conditions are the same as those described in Example 1B.

C. *Preparation of the polyurethane.*
On running the prepolymer described in 4B into the polyester of Example 4A, 1,111 parts of a polyurethane with a relative viscosity, measured as previously indicated, of 3.13, are obtained.

EXAMPLE 5.

A. *Preparation of the polyester.*
A polyester is prepared according to the method described in Example 1 from the following constituents:

	Parts	Molar proportions
Dimethyl terephthalate	236.9	10
Ethylene glycol	227.1	30

The polyesterification is finished at 240°C under atmospheric pressure.
250 parts of a polyester are obtained, the properties of the polyester being as follows:

Acid number (I_a)	0.7 mg of KOH/g
Hydroxyl number (I_{OH})	116.1 „
Number-average molecular weight ($\overline{Mn}$)	965

B. *Preparation of the prepolymer with terminal isocyanate groups.*
The prepolymer is prepared from: 3,920 parts of polyethylene glycol of molecular weight 1,500 and 575 parts of toluene diisocyanate (the commercial mixture previously described).
The working conditions are the same as those described in Example 1B.

C. *Preparation of the polyurethane.*
On running the prepolymer described in 5B into the polyester of Example 5A, 4,745 parts of a polyurethane with a relative viscosity, measured as previously indicated, of 2.05, are obtained.
The following summarising Table allows the properties of the polyurethanes obtained to be compared.

POLYESTER

Examples	Molar composition					Properties		
	DMT	AA	DMSIP	EG	R %	I_a	I_{OH}	$\bar{M}_n$
1	5	3.5	1.5	11.5	15	0.5	29.9	3746
2	8.5	0	1.5	25	15	0	57.4	1951
3	8.5	0	1.5	25	15	0	57.4	1951
4	10	0	0	30	0	0	60.9	1839
5	10	0	0	30	0	0.7	116.1	965

DMT : dimethyl terephthalate

AA : adipic acid

DMSIP : dimethylisophthalate 5 sodium sulphonate

EG : ethylene glycol

R % : ratio of the molar quantity of sulphonated diacid to the total molar quantity of diacids involved in the composition of the polyester.

POLYURETHANES

Examples	% composition by weight: Polyester %	PEG $\overline{Mn}$	PEG %	Diisocyanate	Diisocyanate %	Properties: Prepolymer %	Properties: νr
1	62.7	600	26.9	HMDI	10.3	37.2	2.05
2	31.2	4000	63.3	TDI	5.5	68.8	2.1
3	22.6	1500	67.6	TDI	9.8	77.4	2.31
4	22.6	1500	67.6	TDI	9.8	77.4	3.13
5	5.27	1500	82.6	TDI	12.13	94.73	2.05

PEG : polyethylene glycol

HMDI : hexamethylene diisocyanate

TDI : toluene diisocyanate

νr : relative viscosity

We have found that the products of this invention are excellent anti-redeposition, anti-soiling, and anti-static agents when they are used in the presence of a detergent composition for cleaning synthetic fibres.

By anti-soiling agent is meant a product which facilitates the removal of stains from fabrics on which it has been deposited.

It is known that materials containing a sizeable proportion of polyester fibres have a tendency to be very hydrophobic. This property allows greasy stains, deposited on the fabric, to become fixed thereon, and this makes their removal difficult. Another well-known disadvantage of polyester fibres is that during washing the soiling present in the washing bath can be redeposited on the fabric. In addition, polyester fibres become charged with static electricity either whilst being worn, or during the drying operation. One way of remedying these disadvantages is to deposit on the fibres a finish which confers on them a certain hydrophilic character.

We have found that the products of this invention provide a finish conferring the desired hydrophilic character on polyester fibres upon which they are deposited.

The deposition of the products according to the invention can be carried out by any means, in particular in a finishing operation carried out on the raw fabric by padding or spraying after dyeing, or on the textile article after washing by the user. However, following the preferred method, the deposition of the products is carried out during the operations of washing the fabrics, that is to say that the polyurethanes according to the invention are introduced into the detergent compositions.

The products according to this invention can be incorporated into any type of anionic, non-ionic, cationic, ampholytic, or zwitter-ionic detergent composition. These compositions generally contain, in addition to surfactants and builders, a certain number of conventional ingredients in varying quantities, for example agents encouraging foaming or, conversely, allowing control of the foam, such as the polysiloxanes, mineral salts such as sodium sulphate, whitening agents alone or in a mixture with whitening precursors and other anti-redeposition agents such as carboxymethylcellulose, as well as small quantities of perfumes, colouring agents, fluorescing agents and enzymes.

The incorporation of the ingredients can be carried out by any means, such as addition in the form of a solution or an emulsion when atomising or granulating pulverulent compositions or addition in the form of granules to the said compositions.

As the polyurethanes, according to the invention, have an elastomeric character which is the more pronounced the longer the macrodiol chain present in their structure, it is advantageous to fill them with a finely dispersed mineral ingredient, in order to be able to obtain them in the form of a powder, which can more easily be incorporated into the detergent compositions.

The most appropriate fillers are highly dispersed products, made up of very fine particles, and having a high absorption capacity. Among the appropriate fillers there may be mentioned kaolin, sodium aluminosilicates and silica.

The preferred fillers, according to the present invention, are synthetic silica or sodium aluminosilicates, which are products obtained by precipitation, according to known methods. These fillers are neutral or slightly basic, they are made up of elementary particles whose diameter generally varies from 50 to 1,000 Å and generally have a specific surface area, measured by the BET method, of 50 to 600 m^2/g. Moreover these fillers generally have a porosity of from 50 to 200 cc/100 g, measured with a mercury porosity measuring apparatus, with pore diameters generally varying from 400 Å to 2.5μ.

Their oil adsorption measured using dioctyl phthalate, which is greater than 70 cc/100 g, can be as much as 250 cc/100 g in the case of the sodium aluminosilicates and 460 cc/100 g in the case of silica.

In general, 10 to 90 parts by weight of filler can be used per 90 to 10 parts by weight of polyurethane. Preferably 40 to 70 parts by weight of inorganic filler are impregnated with 60 to 30 parts by weight of the polyurethane, in order to obtain a powder or granules sufficiently dispersible in water, without however leading to too high a level of insoluble materials in the wash liquor.

In order to fill the polyurethane with mineral ingredients, it is possible to melt the polymer first, add the desired quantity of filler and then finely grind the product thus obtained. In the case of polyurethanes with sufficient hydrophilic character to form an aqueous dispersion containing 15 to 20% by weight of the said polyurethanes, it is possible first to prepare a solution or an emulsion of the said polyurethanes, incorporate the desired quantity of filler and then dry and finely grind the product obtained.

This is especially the case with products containing ionic groups whose role is to facilitate the production of a concentrated aqueous dispersion.

In general the polyurethanes according to the invention, are used at the rate of 0.1 to 5% by weight in the detergent compositions. Preferably, 0.5 to 3% by weight of polyurethanes is used in the said compositions.

We have found that the polyurethanes according to the invention, when incorporated into a detergent powder and stored under conditions close to real conditions, generally show, when washing synthetic fibres, a greater effectiveness than products known hitherto to those skilled in the art.

The Examples given below illustrate the use of the products according to the invention and demonstrate the remarkable properties of the said products when they are used as anti-redeposition and anti-soiling agents.

The mineral filler used in the Examples is a product sold by Société SIFRANCE, under the Registered Trade Mark "TIX—O—SIL" 38. It is a synthetic silica, obtained by precipitation.

The following Example illustrates how the polyurethanes according to the invention can be converted to a powder. The parts are expressed by weight.

EXAMPLE 6.

A. *Converting a pre-melted polyurethane to a powder.*

1,000 parts of TIX—O—SIL 38 are heated to 200°C, in a ball mill, under an atmosphere of nitrogen. 1,000 parts, for example, of previously melted polyurethane prepared in Example 3 or 4 are added.

A finely divided powder is thus obtained.

B. *Converting a polyurethane, pre-dispersed in water, to a powder.*

1,000 parts, for example, of polyurethane prepared in Example 1 or 2 are run into 4,000 parts of water maintained at a temperature of 60°C, whilst agitating vigorously. The whole is transferred into a mixer and 1,000 parts of TIX—O—SIL 38 are added. The paste obtained is dried in a ventilated oven at 60°C before being ground.

In the following Example, the storage stability of polyurethanes according to the invention is demonstrated.

EXAMPLE 7.

The products according to the invention are incorporated in the proportion of 3% by weight into the following detergent composition:

Linear alkylbenzenesulphonate (alkyl containing approximately 12 carbon atoms)	9.9%
Alcohol containing 16 to 18 carbon atoms condensed with approximately 15 ethylene oxide units	5 %
Natural tallow soap	6.6%
Sodium tripolyphosphate	34 %
Sodium *ortho*phosphate	0.9%
Sodium pyrophosphate	2.3%
Sodium perborate	22.9%
Sodium sulphate	4.8%
Sodium disilicate	5.4%
Carboxymethylcellulose	0.6%
Water	7.6%

The products according to the invention are filled with the TIX—O—SIL 38 silica, as previously described. The powder obtained is then incorporated into the detergent composition, described above, in a HENRY mixer. The resulting mixture is then stored in an oven maintained at a temperature of 40°C, for 4 weeks.

The stability of the polyurethanes, according to the invention, is then tested in the following manner:

2 strips (20×115 cm) of polyester/cotton (67/33) fabric of reflectance C are washed in a "Miele" (Registered Trade Mark) 421 S automatic machine (colour programme — 60°C) in the presence of 5 g/l of the detergent composition containing the polyurethane in question. The strips of fabric are subsequently dried at ambient temperature and cut up into squares (12×12 cm) onto which are deposited used engine oil, Spangler soiling agent (see J. Am. Oil Chem. 1965—42, 723—727), tomato concentrate and lipstick, 6 squares being used for each type of stain. The stains are then aged by leaving them for one hour in an oven at 60°C. Their reflectance R is measured on an Elrepho apparatus with an FMY/C filter for the engine oil and the Spangler soiling agent and an FMX/C filter for the tomato concentrate and the lipstick.

Thereafter the stained squares are tacked onto ten clean cotton dusters, then washed as before and dried. Their reflectance R_1 is then measured. The effectiveness E as an anti-soiling agent, of the product tested is assessed from the percentage of stains removed calculated by the formula:

$$E \text{ in } \% = \frac{R_1 - R}{C - R} \times 100$$

For each product tested, the average of the percentage removal of different stains is calculated. The results of these tests are recorded in the Table below:

Polymer tested	PU_3			PU_4
X %	83.5	66.5	50	55.5
I	74	74	74	74
F	73	73	67	66

PU_i : indicates the polyurethane described in the example "i"
X %: indicates the amount by weight of TIX—O—SIL 38 incorporated into the polyurethane, expressed per 100 parts by weight of mixture (filler+polyurethane)
I : indicates the average of the percentage removal of different stains before storage of the polymer
F : indicates the same percentage, after storage of the polymer for 4 weeks at 40°C.

The following Table demonstrates the advantage resulting from the high molecular weight of the polyurethanes, according to the invention, when they are stored. In this Table νr indicates the relative viscosity of the products tested, these being the polyurethane described in Example 3 (PU) and the polyester described in Example 2 of French Patent 1,401,581 (PE).

Polymer tested	X %	νr	I	F
PE	83.5	1.2	74	66
PU		2.3	74	73
PE	50	1.2	74	59
PU		2.3	74	67

The following Example illustrates the anti-soiling agent properties of the polyurethanes according to the invention, when they are used in an anionic washing agent.

EXAMPLE 8.

Two strips (20×115 cm) of polyester/cotton (67/33) fabric of reflectance C are washed in a Miele 421 S automatic machine (colour programme — 60°C) in the presence of 5 g/l of the detergent composition described in Example 7. The polyurethane product tested is then introduced at the rate of 3% by weight relative to the said composition. The polyurethane products are incorporated either in the form of a 5% strength by weight aqueous solution, or in the form of powder. The strips of fabric are subsequently dried at ambient temperature and cut up into squares (12×12 cm) onto which are deposited used engine oil, Spangler soiling agent, tomato concentrate and lipstick, 6 squares being used for each type of stain. The stains are then aged, leaving them for one hour in an oven at 60°C. Their reflectance R is measured on an Elrepho apparatus with a FMY/C filter for the engine oil and the Spangler soiling agent and a FMX/C filter for the tomato concentrate and the lipstick.

Thereafter the stained squares are tacked onto ten clean cotton dusters, then washed as before and dried. Their reflectance R_1 is then measured. The effectiveness, E, as an anti-soiling agent, of the product tested is assessed from the percentage removal of stains calculated by the formula:

$$E \text{ in } \% = \frac{R_1 - R}{C - R} \times 100$$

For each product tested the average percentage removal of different stains is calculated. The results of these tests are recorded in the Table below:

Polymer tested	Control	PU_1	PU_2	PU_3		PU_4	PU_5	PU
X %	—	50	50	0	50	55.5	66.6	66.6
E %	45	75	75	74	76	74	73	51

The confidence interval associated with this test is 2%.

In this table a comparative polyurethane, indicated by "PU", has been tested. This polymer is prepared according to the general method described in Example 1, the properties of the polymer being as follows:

Composition

— polyester	22.67% by weight
— Polyethylene glycol of molecular weight 1,500	68.02% „
— Toluene diisocyanate (the commercial mixture previously described).	9.31% „

Relative viscosity: 2.63

The polyester is prepared from 10 mols of adipic acid for 30 mols of ethylene glycol, the properties of the polyester being as follows:

Acid number (I_A)	: 0.5 mg of KOH/g
Hydroxyl number (I_{OH})	: 16.5 „
Number-average molecular weight ($\overline{Mn}$)	: 6,590

In the Example below, the anti-soiling agent properties of the products according to the invention, used in a non-ionic washing agent, are demonstrated.

EXAMPLE 9.

The tests are carried out in conditions identical to those described in Example 8, but with the following non-ionic detergent composition:

Alcohol containing 10 to 12 carbon atoms and having an average of 5 ethylene oxide units	9.4%
Sodium tripolyphosphate	31.4%
Sodium *ortho*phosphate	1.1%
Sodium pyrophosphate	7.3%
Sodium perborate	26.2%
Sodium sulphate	15.8%
Sodium disilicate	8.5%
Polysiloxane (anti-foam)	0.3%

The results of these tests are given in the Table below:

Polymer tested	Control	PU_1	PU_2	PU_3		PU_4
X %	—	60	50	0	50	55.5
E %	45	83	81	80	82	83

In the following Example, the anti-redeposition agent properties of the products according to the invention are demonstrated.

EXAMPLE 10.

Squares (12×12 cm) of polyester/cotton (67/33) fabric are washed in a "Lini-Test" (Registered Trade Mark) apparatus (ORIGINAL HANAU) for 20 minutes at 60°C in hard water (33 French degrees of hardness) containing 0.75 g/l of the following conventional detergent composition:

Linear alkylbenzenesulphonate (alkyl containing approximately 12 carbon atoms)	8 %
Alcohol containing 16 to 18 carbon atoms condensed with approximately 50 ethylene oxide units	3 %
Natural tallow soap	4 %
Sodium tripolyphosphate	30 %
Sodium *ortho*phosphate	1.5%
Sodium pyrophosphate	12.5%
Sodium perborate	25 %
Sodium sulphate	10 %
Sodium disilicate	6 %

Spangler soiling agent is introduced into each washing pot in the proportion of 5% relative to the weight of detergent solution. The product according to the invention is tested at the rate of 3% by weight relative to the detergent composition into which it is incorporated.

The redeposition of the Spangler soiling agent on the fabric is given by the value R of the reflectance of the fabric washed in the presence of the product according to the invention. The reflectance is measured on a Gardner apparatus (GARDNER INSTRUMENTS). As an indication, the unwashed fabric has a reflectance equal to 85.6.

The results obtained with a certain number of products described above are given in the Table below:

Polymer tested	Control	PU_1	PU_2	PU_3		PU_4
X %	—	50	50	0	50	55.5
R	67	79.2	78.4	82.0	82.4	81

The confidence interval, under the test conditions is 1.

In the following Example, the antistatic agent properties of the products according to the invention are demonstrated.

EXAMPLE 11.

Two strips (20×115 cm) of polyester fabric ("Dacron" [Registered Trade Mark] type 54 TEST FABRICS INC.) are washed in a Miele 421 S automatic machine (colour programme — 60°C) in the presence of 5 g/l of the detergent composition described in Example 7. The polyurethane product tested is introduced at the rate of 3% by weight relative to the detergent composition in which it is incorporated. The fabric strips are then dried at ambient temperature and cut into discs of 10 cm diameter. The fabric discs are then conditioned for 24 hours in a chamber in which the temperature and the degree of humidity are controlled (22°C; 46% RH). Each of the samples is charged electrostatically, and the time of half discharge and three-quarters discharge is then measured using an electrostatic charge meter (Creusot-Loire).

Product tested	Control	PU_2
X %	—	50
Half-discharge in seconds	180	5
3/4 discharge in seconds	1,440	20

WHAT WE CLAIM IS:—

1. A process for preparing a linear, hydrophilic polyurethane of relative viscosity (as hereinbefore defined) of at least 2, which comprises reacting 5 to 70% by weight of a linear hydroxyl-terminated polyester derived from terephthalic acid or a diester thereof, said polyester having a hydroxyl number of not more than 120 mg of KOH/g and an acid number of at most 3 mg of KOH/g, with 95 to 30% by weight of a prepolymer with terminal isocyanate groups, obtained by reacting at least one polyethylene glycol with at least one diisocyanate, the overall molar ratio NCO/OH being at least 0.8 but less than 1.

2. A process according to claim 1 in which the number-average molecular weight of the polyester is from 1,000 to 4,000.

3. A process according to claim 1 or 2 in which the polyethylene glycol has a number-average molecular weight from 300 to 6,000.

4. A process according to claim 3 in which the number-average molecular weight of the polyethylene glycol is from 600 to 4,000.

5. A process according to any one of the preceding claims, in which the diisocyanate is hexamethylene diisocyanate, toluene diisocyanate, di-(isocyanatophenyl)-methane or isophorone diisocyanate.

6. A process according to claim 5 in which the diisocyanate is used in an amount from 2 to 15% by weight relative to the weight of the polyurethane produced.

7. A process according to any one of the preceding claims in which the polyester is obtained from terephthalic acid or a diester thereof, and at least one of ethylene glycol, diethylene glycol or a higher homologue thereof of molecular weight at most 300, butane-1,4-diol or propane-1,2-diol.

8. A process according to claim 7, in which the polyester is obtained from a mixture of terephthalic acid or a diester thereof, and adipic acid or a diester thereof, as the acid component.

9. A process according to claim 7 or 8 in which during the preparation of the polyester 5-sulphoisophthalic acid or its methyl diester is introduced in the form of an alkali metal salt, the molar proportion of the sulphonated diacid relative to the total molar quantity of diacids involved in the preparation of the polyester being not more than 15%.

10. A process according to any one of the preceding claims which comprises reacting 10 to 70% by weight of the polyester with 90 to 30% by weight of the prepolymer.

11. A process according to claim 1 substantially as hereinbefore described.

12. A process according to claim 1 substantially as described in any one of Examples 1 to 4.

13. A process according to claim 1 substantially as described in Example 5.

14. A linear, hydrophilic polyurethane whenever prepared by a process as claimed in any one of claims 1 to 13.

15. A detergent composition which comprises a polyurethane as claimed in claim 14 as an anti-redeposition, anti-soiling or antistatic agent.

16. A composition according to claim 15 which contains 0.1 to 5% by weight of the polyurethane.

17. A composition according to claim 15 or 16 which comprises granules containing 40 to 70 parts by weight of inorganic filler and, correspondingly, 60 to 30 parts by weight of the polyurethane.

18. A composition according to claim 17 in which the filler is silica or a sodium aluminosilicate.

19. A composition according to claim 15 substantially as hereinbefore described.

20. A composition according to claim 15 substantially as described in any one of Examples 7 to 11.

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